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# Engineered pellets from dry torrefied and HTC biochar blends

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## ARTICLE INFO

### Article history:

Received 10 April 2013

Accepted 31 January 2014

Available online 28 February 2014

### Keywords:

Torrefaction

Pelletization

Hydrothermal carbonization

Biomass densification

Loblolly pine

## ABSTRACT

Dry torrefaction and hydrothermal carbonization (HTC) are two thermal pretreatment processes for making homogenized, carbon rich, hydrophobic, and energy dense solid fuel from lignocellulosic biomass. Pellets made from torrefied biochar have poor durability compared to pellets of raw biomass. Durability, mass density, and energy density of torrefied biochar pellets decrease with increasing dry torrefaction temperature. Durable pellets of torrefied biochar may be engineered for high durability using HTC biochar as a binder. In this study, biomass dry torrefied for 1 h at 250, 275, 300, and 350 °C was pelletized with various proportions of biomass HTC treated at 260 °C for 5 min. During the pelletization of biochar blends, HTC biochar fills the void spaces and makes solid bridges between torrefied biochar particles, thus increasing the durability of the blended pellets. The engineered pellets' durability is increased with increasing HTC biochar fraction. For instance, engineered pellets of 90% Dry 300 and 10% HTC 260 are 82.5% durable, which is 33% more durable than 100% Dry 300 biochar pellets, and also have 7% higher energy density than 100% Dry 300 biochar pellets.

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## 1. Introduction

There are two widely known thermal pretreatment technologies, known as hydrothermal carbonization (wet torrefaction) and dry torrefaction. In dry torrefaction, also known as torrefaction or mild pyrolysis, dry solid biomass is treated in an inert gas environment in a temperature range of 200–300 °C for more than 1 h [1–3]. In hydrothermal carbonization (HTC), biomass is treated with hot compressed subcritical water (200–260 °C) for 5 min–8 h. The solid product, HTC biochar, contains about 55–90% of the mass and 80–95% of the fuel value of the original feedstock [1,4,5]. Both processes produce solid products that exhibit increased energy density and that are easily friable and much more hydrophobic relative to the original biomass [6,7,9].

Although both thermal pretreatment processes improve biomass energy value, both dry torrefied biochar and HTC biochar are friable and still hard to handle [2,8]. Pelletization offers further densification of the mass and energy of biochar, and the pellets' uniform shape makes them easier to handle. Pelletization in general depends on various properties such as temperature, moisture content, biomass type, binder, and pelletizer type, along with compression force or pressure [10]. Beyond its glass transition temperature, binder develops liquid bridges between adjacent particles. In most cases, an immobile thin adsorption layer is produced by the binder. This layer attaches the particles by effectively reducing surface roughness or decreasing inter-particle distance, with attractive forces then resulting in binding and the formation of stable bonds [11]. Liquid bridges are then converted to solid bridges with

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<http://dx.doi.org/10.1016/j.biombioe.2014.01.038>

decompression and reduction of the temperature to ambient. Lignin in raw wood serves as an excellent pellet binder.

Dry torrefied biochar has an increased energy densification, but is difficult to pelletize [12–15]. Pure dry torrefied biochar pellets have very low durability and mass density [14]. As a result, dry biochar pellets have similar or lower energy density compared to raw pine pellets. An appropriate binder could improve the energy density and durability of dry torrefied biochar. Both raw pine and pine pretreated in liquid water at 260 °C (henceforth called HTC 260) have enough available natural binder and their pellets show promising evidence of solid bridge formation when pelletized at 140 °C [15]. Raw biomass binder (generally hemicellulose, lignin, and moisture) is weaker than HTC 260 biochar binder (modified lignin) [15]. Moreover, raw biomass is hydrophilic and subject to biodegradation in prolonged storage.

Large-scale industrial providers of biomass pellets are concerned with pellet durability when exposed to liquid water. Pellets produced from raw loblolly pine break apart within 30 s after immersion in liquid water [16]. The decay is so rapid that no pellet is observed, only a mound of biomass. Pellets produced under identical pelletizing conditions of time, temperature, and pressure from HTC biochar or/and dry torrefied biochar perform quite well when immersed in liquid water, mainly due to the hydrophobic nature of both biochars [17–19].

The higher heating value (HHV) of raw pine is lower than that of dry torrefied biochar; as a result blended pellets of the two would be expected to have lower energy yield along with better durability compared to pellets made only from torrefied biochar. So, using a raw biomass binder may reduce the dry torrefied pellets' energy density and give the pellet a tendency to deteriorate in water. In contrast to raw pine, HTC 260 biochar is more hydrophobic, its lignin can make very stable solid bridges resulting in very high durability, and it has a larger HHV [1,15,17]. An important drawback to using HTC 260 biochar is its cost of production [9]. HTC practice is currently limited to batch processes, and its requirement for high pressures and temperatures makes continuous HTC processing challenging. So, a pellet made from a blend of primarily low-cost dry torrefied biochar, and a small amount of HTC biochar added as binder, may exhibit desirable properties of density, durability, and cost.

The main objective of the present study is to characterize engineered pellets of dry torrefied biochar with HTC biochar added as a binder. Chemical differences between dry torrefied and HTC biochar were analyzed. The effect of temperature on fuel and pelletizing properties of dry torrefied biochar was examined. Optimization of the HTC 260 biochar binder concentration in engineered pellets was explored, considering fuel properties, durability, and storage capability.

## 2. Materials and methods

### 2.1. Biomass and chemicals

Loblolly pine (*Pinus taeda*) was used for all experiments. Mature loblolly pine was harvested in Marengo County, Alabama in May 2011. Wood stems were debarked and

comminuted into wood chips. The material was dried in a warehouse by free air circulation for four weeks and further chopped into particles <15 mm by Bliss hammermill model 4460 (Ponca City, OK). Harvested biomass were dried in a warehouse by free air circulation for a month and stored in plastic container in a dry storage until further use. To promote a more homogeneous biomass reactant and provide effective sub-critical water diffusion in the biomass, a blender was used to reduce the raw biomass size. Samples were sieved to  $-1.18\text{ mm} + 0.60\text{ mm}$ , air dried, and stored in a sealed ziplock bag until treatment. The pelletizing equipment, a 15 Mt hydraulic press and a heated die with a temperature controller, was purchased from Across International (New Providence, NJ). It can operate at temperatures up to 250 °C with an accuracy of  $\pm 1\text{ }^{\circ}\text{C}$ .

### 2.2. Dry torrefaction

Dry torrefaction of loblolly pine was performed in a 100 cm<sup>3</sup> Parr bench-top reactor (Moline, IL) at temperatures ranging from 250 to 350 °C. A glass liner was used to prevent contact of the biomass with the reactor's hot metal surface. Approximately 5 g of dried loblolly pine was placed in the center of the reactor. Nitrogen was kept flowing continuously at the rate of 20 cm<sup>3</sup> (STP) min<sup>-1</sup>. The torrefaction temperature was selected to be 250, 275, 300, or 300 °C using a reaction time of 60 min for each run. Nitrogen flow was stopped after 60 min of torrefaction. The reactor was rapidly cooled down to room temperature by immersing it in an ice-water bath and solid samples were collected for further analysis, with the temperature lowered to less than 180 °C in 2 min. Dry 250, Dry 275, Dry 300, and Dry 350 biochar were the dried solid products of dry torrefaction at the temperatures 250 °C, 275 °C, 300 °C, and 350 °C, respectively.

### 2.3. Hydrothermal carbonization

Hydrothermal carbonization of loblolly pine was performed in a 100 cm<sup>3</sup> Parr bench-top reactor (Moline, IL). Nitrogen of 80 cm<sup>3</sup> (STP) min<sup>-1</sup> was first passed through the reactor for 10 min to purge oxygen. For each run, a 1:5 weight basis mixture of loblolly pine and water was loaded into the reactor. The reactor was heated to 260 °C and maintained at that temperature for 5 min using a PID controller. The reactor pressure was not controlled but indicated by the pressure gauge to be approximately 4.6 MPa at 260 °C. After remaining for 5 min at 260 °C, the reactor was cooled rapidly by immersing it in an ice-water bath. The gas generated was released to the atmosphere. The solid product was filtered from the liquid and put in a drying oven at 105 °C for 24 h before further analysis. HTC 260 biochar was the dried solid product of hydrothermal carbonization at 260 °C.

### 2.4. Fiber analysis

The van Soest method of NDF-ADF-ADL (neutral detergent fiber, acid detergent fiber, acid detergent liquid) dissolution was used to determine the percentage of hemicelluloses, cellulose, and lignin in solid samples [20]. The contents of hemicelluloses, cellulose, and lignin were calculated from the

difference of NDF, ADF, ADL, and ash. Sample mass that is not assigned to one of those fractions consists of what are called extractives, which are aqueous soluble polysaccharides, saccharides, proteins, starch, and other components. Samples were dried at 105 °C for 24 h prior to fiber analysis. Ash, determined separately by muffle furnace, subtracted from lignin and ash weight from fiber analysis, to find lignin content. So, lignin is not measured directly and this is one of the main shortcomings of this method. Biomass is divided into five components only in this method and any change of one component will effect the others.

## 2.5. Differential scanning calorimetry (DSC)

The ash content of loblolly pine is very low, less than 1% of biomass, even for dry torrefied biochar and HTC biochar [1]. So, it is reasonable to assume that the residue from the fiber analysis of HTC biochar is lignin or a derivative of lignin. An STA-6000 from Perkin Elmer (MA, USA) was used to determine the thermal behavior of lignin derived from HTC biochar, and to identify a glass transition temperature. Derived lignin obtained from fiber analysis was dried at 105 °C for 24 h prior to the DSC-TGA analysis. Samples of 10–15 mg were placed into the sample chamber. The sample mesh size was 0.5–0.7 mm. Gaseous nitrogen of 20 cm<sup>3</sup> min<sup>-1</sup> was charged to ensure an inert atmosphere. The heat cycle applied was 30–200 °C at a rate of 5 °C min<sup>-1</sup> for the entire temperature scan.

## 2.6. Attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR)

A Perkin–Elmer Spectrum 2000 ATR-FTIR with mid- and far-IR capabilities was used on the raw and pretreated biomass. IR spectra of Dry 250, Dry 275, Dry 300, and Dry 350 biochars, as well as HTC 260 and raw loblolly pine, were recorded at 30 °C using ATR-FTIR. All samples were milled into fine powder to homogenize them and dried in 105 °C for 24 h in an oven prior to FTIR. Only 5–10 mg of dry sample was placed in the FTIR for this analysis and pressed against the instrument's diamond surface with its metal rod. All spectra were obtained using 200 scans for the background (air) and 32 scans for the samples, which were scanned from 500 to 4000 cm<sup>-1</sup>.

## 2.7. Pelletization technique

The HTC biochar was exposed to ambient conditions for 3 weeks prior to pelletization to stabilize the moisture content. Moisture contents of raw, Dry 250, Dry 275, Dry 300, Dry 350, and HTC 260 biochar were 8.3%, 2.5%, 1.1%, 0.7%, 0.5% and 4.2%, respectively, prior to pelletizing. Approximately 1 g of the pretreated biomass was placed manually into a die of 13 mm diameter. A 500W band heater was used to heat the sample with a controller maintaining the temperature of the sample at about 140 °C. A compressive force of 250 MPa was applied to the sample by a lever. After a holding time of 30 s, the pressure was released and the heater was turned off simultaneously. The pellet was removed from the die and left undisturbed for 2–5 min. It was then stored at room temperature before further analysis. The L:D ratio of the pellets ranged from 0.6 to 0.75 in this study.

## 2.8. Durability

To evaluate the durability or mechanical strength of the pellets, the MICUM test [16,22], which is popular for characterizing coal, was adapted here. The rotating drum technique as a durability test is common in the literature [14,22]. Exactly 10 pellets were charged into a cylindrical rotating drum with an inner diameter of 101.6 mm and a length of 95 mm. Two baffles of 25.4 × 88.9 mm were installed opposite to each other and perpendicular to the cylinder wall. The drum rotated at 38 revolutions per min. After 3000 revolutions, the sample was screened using a 1.56 mm sieve. Particles that fell through the screen were then weighed. Durability is the ratio of mass larger than 1.56 mm after 3000 rotations to the initial sample mass. The higher the durability, the better quality is the pellet.

## 2.9. Scanning electron microscopy (SEM)

A FE-SEM Hitachi Scanning Electron Microscope (SEM) model S-4700 was used to study the bonding mechanism of the engineered pellets by fracture surface analysis of failed pellets. Pellets of raw pine, Dry 300 biochar, HTC 260 biochar, and the engineered pellets of blends of HTC 260 and Dry 300 biochar were examined in SEM. The samples were dried in a 105 °C oven for 24 h prior to analysis. Each pellet was manually cracked into two parts. A tiny notch was cut in the center of each pellet using a surgical blade and each pellet was carefully snapped into two halves. Each pellet half was maintained on special studs and platinum coated with polaron coater tar 5000, under an argon atmosphere for a coating thickness of approximately 1000 Å. A voltage of 15–20 kV with a magnification of 50–500 times was used for the images. Multiple samples were observed for each pellet and the best representative images were chosen for each sample type.

# 3. Results and discussion

## 3.1. Fiber analysis of dry and HTC biochar

Raw loblolly pine has 8.9% extractives, 11.8% hemicelluloses, 54% cellulose, 25% lignin and a small amount (0.4%) of ash [Table 1]. Water extractives and hemicellulose fractions decrease with increasing dry torrefaction temperature. In fact, there are almost no extractives or hemicelluloses found in Dry 350 or Dry 300. Cellulose degradation has been reported to require a higher torrefaction temperature than that required for hemicelluloses or extractives [24,25]. As shown in Table 1, significant cellulose degradation occurred only at a dry torrefaction temperature greater than 275 °C. An increase of dry torrefaction temperature above 275 °C degrades cellulose quite drastically, in fact, cellulose percentage decreases from 52.7% for Dry 275 to 18% for Dry 350 biochar. With increasing dry torrefaction temperature a trend toward increased lignin percentage was found. Lignin itself is not produced during the dry torrefaction process; rather, the degradation of hemicellulose and extractives increases the lignin percentage. However, when cellulose undergoes dry torrefaction pretreatment, it can yield a cross-linked solid residue [8], indistinguishable from lignin using the van Soest method [21]. For this reason,

**Table 1 – Fiber analysis, mass yield, and energy values of dry and HTC biochar.**

| Condition | Extractives (%) | Hemicellulose (%) | Cellulose (%) | Lignin (%) | Ash (%) | Mass yield (%) | HHV (MJ kg <sup>-1</sup> ) |
|-----------|-----------------|-------------------|---------------|------------|---------|----------------|----------------------------|
| Raw       | 8.9             | 11.8              | 54            | 25         | 0.4     | 100            | 19.5 ± 0.5                 |
| Dry 250   | 5.5             | 9.2               | 51            | 34.1       | 0.5     | 84 ± 0.5       | 20.9 ± 0.6                 |
| Dry 275   | 3.2             | 6.5               | 52.7          | 36.7       | 0.6     | 74 ± 1.0       | 21.8 ± 0.5                 |
| Dry 300   | 2.2             | 2.3               | 32.7          | 62.7       | 0.7     | 61 ± 0.6       | 23.5 ± 0.8                 |
| Dry 350   | 1               | 0                 | 18            | 80         | 0.9     | 48 ± 1.2       | 29.9 ± 0.7                 |
| HTC 260   | 31.8            | 0                 | 33.9          | 33.8       | 0.6     | 54 ± 0.5       | 26.5 ± 0.4                 |

an increase in lignin percentage is observed for Dry 300 and Dry 350 biochar. Raw loblolly pine has very low ash, which is unaffected by dry torrefaction. As a result, the ash percentage increases slightly with dry torrefaction severity, i.e., with decreased mass yield.

During dry torrefaction, water extractives and hemicellulose degrade into volatile products leaving very small or no solid residue [18]. Cellulose yields at least 35% as solid biochar, while the rest becomes volatiles or gases [1,30]. Thus, biomass weight is reduced during dry torrefaction. For this reason, a decreasing trend in mass yield (i.e., yield of solid biochar product) was observed with increasing dry torrefaction temperature, as shown in Table 1. In fact, the biomass lost more than 50% of its original mass during dry torrefaction at 350 °C. These results are consistent with previous studies [1,3,5,19]. Higher heating values (HHV) of raw loblolly, dry torrefied biochar, and HTC biochar are also listed in Table 1. Energy values depend on the elemental carbon content compared to the elemental oxygen content of the biomass and thus HHV for components follow this simple trend; ash < extractives < hemicellulose < cellulose < lignin [21]. Therefore, an increasing trend for HHV with increasing dry torrefaction temperature was observed. HHV of Dry 350 is about 53% more than HHV of raw pine.

In hydrothermal carbonization, subcritical water is used because its ionic constant is increased nearly two orders of magnitude and liquid water behaves as a non-polar solvent at temperatures of 200–280 °C [7,26]. In other words, subcritical liquid water is very reactive and efficient in breaking the β-(1–4) glycosidic bonds of hemicellulose, and cellulose [7,21]. It can also hydrolyze the extractives very quickly [7]. Consequently, only a 5 min pretreatment at 260 °C proves very effective for degradation of hemicellulose, extractives, and a fraction of cellulose (Table 1) [16,30]. The mass yield of HTC 260 is lower than the mass yield of Dry 300. During HTC, biomass components (hemicellulose, cellulose, and extractives) degrade into sugar monomers, which further react to form furfurals and other energy rich compounds, including 5-HMF (hydroxyl methyl furfural) [5,23]. Such compounds may precipitate into the HTC biochar pores. Due to the degradation of lower energy valued hemicellulose and cellulose during HTC, the HHV of HTC 260 biochar is 12.7% higher than Dry 300 biochar's HHV and 35.9% higher than that of raw biomass.

### 3.2. Glass transition behavior of dry and HTC biochar

Glass transition behavior is a unique characteristic of natural binders. Lignin and hemicellulose are the two major components that show natural binding ability in biomass [27]. Feed containing a higher percentage of lignin and hemicellulose

shows better binding characteristics with compression under conditions higher than their glass transition temperatures. To determine glass transition behavior precisely, the derivative of heat flow with respect to temperature, as measured in the DSC, is plotted versus treatment temperature (Fig. 1). The lignin extracted from raw loblolly pine (Fig. 1(a)) and lignin extracted from HTC biochar (Fig. 1(b)) both show a range of glass transition temperatures between 135 and 165 °C in the heat flow versus temperature curve, which is consistent with the literature [15,31]. The same range of glass transition temperature indicates the similarity of the lignin from the raw biomass to that of HTC 260 biochar. It might be expected that pellets made from both feedstocks (raw pine and HTC 260 biochar) might exhibit similar qualities for durability.

Extracted lignin from various dry torrefied biochars does not show glass transition behavior in the temperature range of 25–200 °C. According to van Soest fiber analysis, the

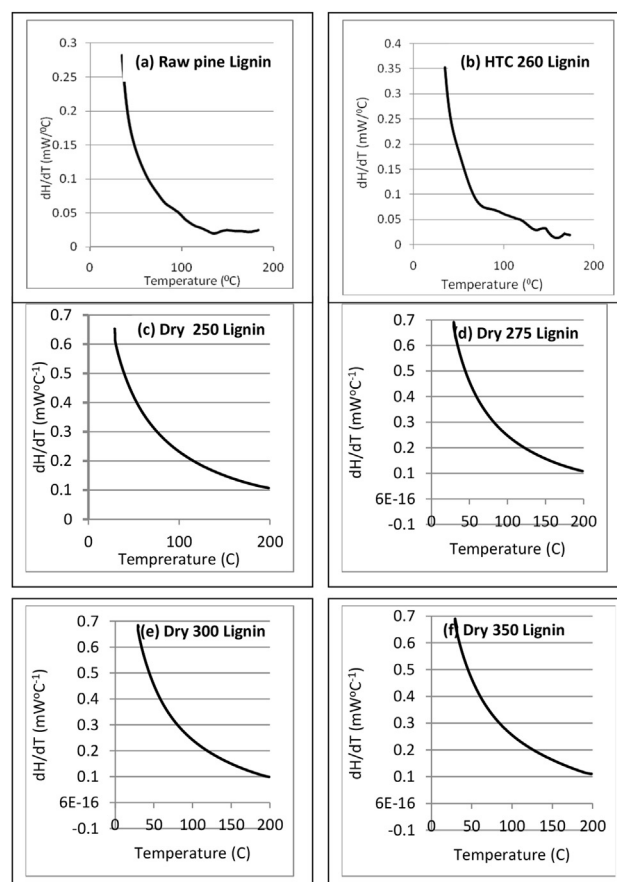


**Fig. 1 – Differential DSC curves for dry torrefied biochars, HTC 260 biochar and raw pine.**

content of lignin increases in these biochars with increasing dry torrefaction temperature. In fact, Dry 300 and Dry 350 have 65.2% and 80% lignin, respectively, in their biochars, and yet there is no sign of glass transition behavior in Fig. 1(e, f). As described earlier in Section 2.4, lignin is not measured directly using the van Soest method, but calculated from the undissolved residue of ADL treatment. The lignin may be altered structurally when dry torrefied, losing its glass transition behavior. However, lignin derived from the HTC biochar shows similar glass transition behavior to that of raw biomass (Fig. 1(b)). This suggests that lignin may be unaffected by HTC, which is consistent with a previous study [15]. This glass transition behavior indicates that lignin in raw biomass and HTC biochar is a viable endogenous binder for pelletization at a temperature of 140 °C.

### 3.3. FTIR analysis of dry and HTC biochar

Dry torrefied biochar does not show any glass transition behavior, although a higher proportion of lignin-like compounds was observed in dry torrefied biochar compared to raw or even HTC biochar (Section 3.2). This may be an indication that lignin is chemically changed during dry torrefaction and so loses its binding capability. The changes in chemical bonds present in the biomass were studied following dry torrefaction and HTC using ATR-FTIR spectroscopy and are presented in

Fig. 2. Table 2 identifies functional groups at particular wavelengths and the corresponding chemical compounds.

From Fig. 2, raw loblolly pine shows strong bonds at 910, 1050, 1180, 1260, 1390, 1510, 1613, and 1735  $\text{cm}^{-1}$  in the fingerprint region. These correspond to aromatic carbon hydrogen bonds of hemicellulose (C–H), alcohol groups of glucose (C–OH), glycosidic bonds of cellulose (C–O–C), aryl-alkyl ethers of lignin (O–CH<sub>3</sub>), aromatic acids of hemicelluloses (C–H), ketone groups of hemicelluloses (C=O), aromatic carbon skeletons (C=C), and carboxylic acid groups of hemicellulose (C=O) respectively. A broad aliphatic hydrocarbon or wax (–CH) and aliphatic hydroxyl bond for bound water (–OH) can be observed at 2840–2920, and 3100–3500  $\text{cm}^{-1}$  respectively [12]. The intensity of the broad band for aliphatic –OH (3100–3500  $\text{cm}^{-1}$ ) decreases with increasing dry torrefaction temperature especially at temperatures of 300 °C or higher. As a result, the dry torrefied biochar displays increased hydrophobicity with higher dry torrefaction temperatures, explaining effects on equilibrium moisture content reported elsewhere [1,17]. Aliphatic –CH remains unchanged by dry torrefaction in the 250–350 °C temperature range. Vibration at about 1735  $\text{cm}^{-1}$ , which is representative of hemicellulose, is shifted gradually with increasing dry torrefaction temperature to 1694  $\text{cm}^{-1}$ . Xyloglucan, arabinoglucuronoxylan, actoglucomanan, and other hemicellulose compounds are degraded with increasing dry torrefaction temperature [28]. This is consistent with the van

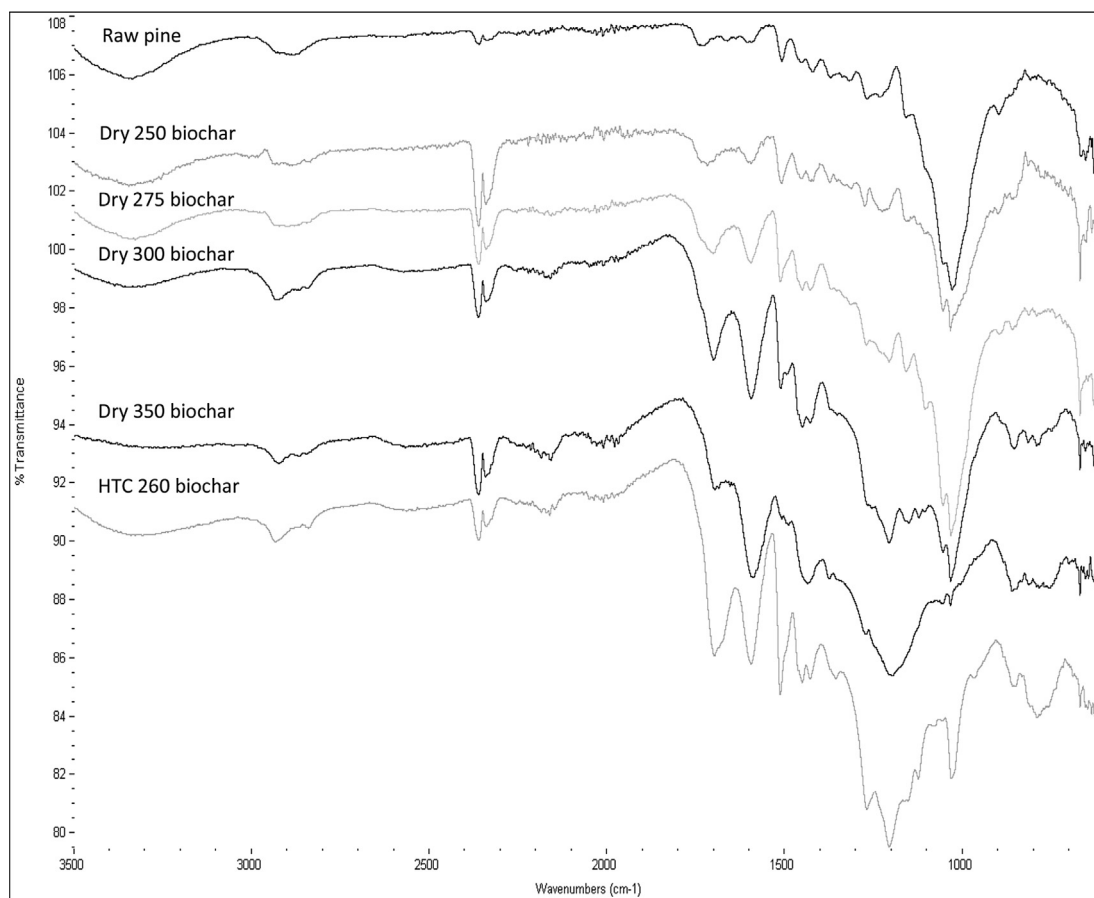


Fig. 2 – IR spectra of various dry torrefied biochar along with raw pine and HTC 260 biochar (vertical axis has arbitrary unit).

**Table 2 – IR absorption corresponding to various functional groups [18,28,29].**

| Wave number (cm <sup>-1</sup> ) | Functional groups                  | Possible compounds         |
|---------------------------------|------------------------------------|----------------------------|
| 3600–3000                       | OH stretching                      | Acid, methanol, water      |
| 2860–2970                       | C–H <sub>n</sub> stretching        | Alkyl, aliphatic, aromatic |
| 1700–1730                       | C=O stretching                     | Ketone and hemicellulose   |
| 1510–1560                       | C=C                                | Lignin                     |
| 1632                            | C=C stretching                     | Cellulose, Lignin          |
| 1613, 1450                      | O–CH <sub>3</sub>                  | Lignin                     |
| 1470–1430                       | OH bending                         | Acid                       |
| 1440–1400                       | CH bending                         | Acid                       |
| 1402                            | C–O–C stretching                   | Cellulose                  |
| 1232                            | C–O stretching                     | Lignin                     |
| 1215                            | C–O–C stretching vibration         | Cellulose                  |
| 1170, 1082                      | OH association                     | Alcohol, hemicellulose     |
| 1108                            | C–O stretching and C–O deformation | Alcohol                    |
| 1060                            | C–H                                | Cellulose, hemicellulose   |
| 700–900                         | C–H                                | Hemicellulose              |

Soest fiber analysis results discussed in Section 3.1, where no hemicellulose was found in Dry 350. A decreasing intensity of the bands (C–O–C) corresponding to cellulose at 1160 and 1194 cm<sup>-1</sup> was observed with increasing dry torrefaction temperature, which is also consistent with Section 3.1. Specific lignin vibrations can be found at about 1260 cm<sup>-1</sup> due to methoxyl bonds, and also at about 1420, 1450, 1490, and 1510 cm<sup>-1</sup> due to C=C bond in the pyranose ring of lignin [20,28]. The intensities of the bands at about 1420, 1440, and 1490 remain unchanged at dry torrefaction temperatures lower than 300 °C but decrease at higher temperatures. The band at 1260 cm<sup>-1</sup> disappears at dry torrefaction temperatures higher than 275 °C. These changes suggest that lignin is changed chemically during dry torrefaction at higher temperatures. Stelte et al. [12] stated that lignin is to a large extent degraded at temperatures higher than 300 °C during dry torrefaction. So effects of dry torrefaction temperature, including increasing hydrophobicity, decreasing presence of hemicellulose and cellulose, and changes in lignin structure, can be explained by or confirmed by the IR spectra shown in Fig. 2.

The IR spectrum of HTC 260 biochar is different than that of dry torrefied biochar or raw pine. The repetitive bands of hemicellulose are absent in the HTC biochar spectra, moreover, the hemicellulose band (C=O) at 1735 cm<sup>-1</sup> is shifted to 1694 cm<sup>-1</sup>, which corresponds to the aromatic C–H band [29]. Intensities of glycosidic bonds of cellulose are increased in HTC 260 biochar compared to raw or dry torrefied biochar. Intensities of lignin bands around 1420 and 1440 cm<sup>-1</sup> are similar to those of raw pine, Dry 250, Dry 275, and Dry 300. Vibration bands at 1260 and 1510 cm<sup>-1</sup> have been shifted to 1275 and 1494 cm<sup>-1</sup>, respectively, shifts which are not present for the dry torrefied biochars' spectra. Although HTC 260 and dry torrefied biochar have some similar bands relating to lignin, distinguishing bands for HTC 260 exist at 1494 and 1275 cm<sup>-1</sup>.

### 3.4. Characteristics of pure dry and HTC biochar pellets

Dry torrefied biochar pellets exhibit characteristics quite different from those exhibited by pellets made from raw pine or from HTC 260 biochar. Durability, mass density, and energy density of pure raw, dry, and HTC biochar pellets are presented in Table 3. Durability of pellets made from dry torrefied loblolly pine decreases rapidly with increasing torrefaction temperature. Dry 350 biochar pellets have a durability of  $9.3 \pm 1.1\%$ , which is less than one tenth that of HTC 260 biochar pellets or even raw pine pellets. Dry 300 torrefied pellets are only  $55.6 \pm 1.2\%$  durable, which is better than Dry 350 pellets but still very poor in durability. Stelte et al. [12] stated that Dry 300 cannot be used to make any pellet. The pelletizing process used there was different, their torrefaction time was twice that used in this study, and a different raw biomass (Norway Spruce) was used. In comparison, Reza et al. [15] reported that Dry 300 biochar pellets from loblolly pine are 79% durable, but a much higher pelletizing pressure was applied in their study, which likely increased durability. Pure HTC 260 biochar pellets are very durable ( $99.8 \pm 0.1\%$ ), which means that HTC biochar has better binding capability, a finding consistent with the literature [15].

Evaluation of SEM images can provide useful insight to understand the failure mechanisms, types of particle binding, and durability of raw biomass, HTC biochar, and torrefied biochar pellets for different biomass types [2,14,15]. SEM images of a raw pine pellet, a Dry 300 pellet, and an HTC 260 pellet at two different magnifications (50× and 500×) are presented in Fig. 3. Raw pine and HTC 260 biochar pellets apparently developed a solid bridge binding between particles, and as a result no visible cracks can be observed. Reza et al. [15] stated that raw pine and HTC 260 biochar pellets have adequate binder from hemicellulose, lignin, and moisture to construct stable solid bridges. The Dry 300 biochar pellet shows cracks of 10 μm and larger, as seen in Fig. 3(f). Previous researchers have found mechanical interlocking among the particles in dry biochar pellets [13,14,18]. Mechanical interlocks in biomass pellets are weaker than solid bridges and, as a result, the dry biochar pellets have less durability [15]. Such cracks are also responsible for the pellets' low mass density, as they increase the void space in the pellet.

For the case of pretreated biomass pellets, Table 3 shows that with increasing dry torrefaction temperature the pellet density decreases, especially when pretreated above 275 °C. Pellets of loblolly pine dry torrefied at 350 °C have a density

**Table 3 – Durability, mass density, and energy density of pellets made from raw pine, 100% dry torrefied biochar, and HTC 260 biochar.**

| Condition | Durability (%) | Mass density (Kg m <sup>-3</sup> ) | Energy density (GJ m <sup>-3</sup> ) |
|-----------|----------------|------------------------------------|--------------------------------------|
| Raw       | $97.5 \pm 0.5$ | $1080.2 \pm 5.1$                   | $21.3 \pm 0.5$                       |
| Dry 250   | $77.3 \pm 0.9$ | $1048 \pm 10.1$                    | $22.3 \pm 0.4$                       |
| Dry 275   | $78.0 \pm 1.0$ | $1012 \pm 6.2$                     | $22.7 \pm 0.6$                       |
| Dry 300   | $55.6 \pm 1.1$ | $931 \pm 6.8$                      | $22.4 \pm 0.7$                       |
| Dry 350   | $9.3 \pm 1.2$  | $689 \pm 10.8$                     | $20.0 \pm 1.1$                       |
| HTC 260   | $99.8 \pm 0.1$ | $1478 \pm 9.7$                     | $39.2 \pm 0.2$                       |

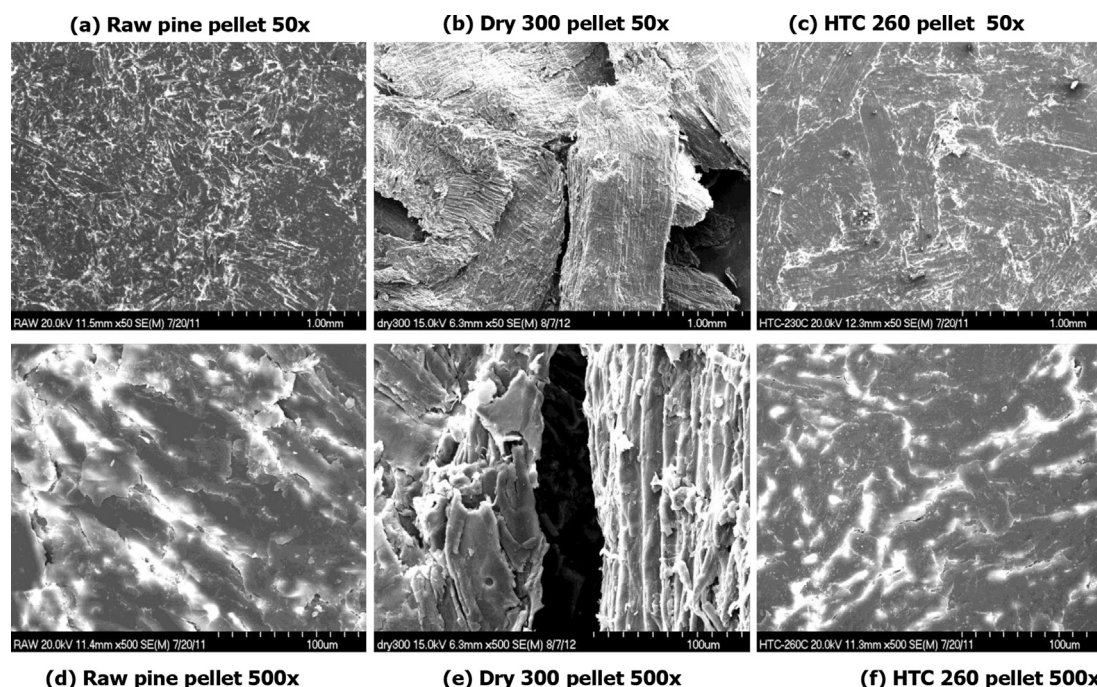


**Fig. 3 – SEM images of raw pine, 100% Dry 300 biochar, and HTC 260 biochar pellets in 50× and 500× magnification.**

which is 36% lower than pellets of raw pine and 0.46 times of HTC 260 biochar pellets. However, Dry 250 and Dry 275 pellets (of similar mass density as raw pine pellets) are more durable than those from Dry 300 and Dry 350 biochar. The mass density of pure HTC 260 biochar pellets is  $1478 \pm 9.8 \text{ kg m}^{-3}$ , which is 27% higher than that of raw pine pellets.

Energy density is the product of mass density and HHV. It is similar for all dry torrefied pellets, except for Dry 350. For Dry 350 pellets, energy density is 11% lower compared to the other dry torrefied pellets and 6% lower compared to raw pine pellets. Energy density is similar for raw and dry torrefied pellets because the increased HHV of the later makes up for their lower mass density. Pellets of HTC 260 biochar have an energy density 84% higher than that of raw pine pellets, 74% higher than Dry 250, Dry 275, or Dry 300 pellets, and 96% higher than Dry 350 pellets, due to its increased mass density and HHV.

### 3.5. Engineered pellets of dry and HTC biochar

Durability of engineered pellets increases with increasing addition of HTC 260 biochar, as shown in Fig. 4. Adding only 10% HTC 260 biochar can improve the engineered pellets durability from 77% to 95% for Dry 250 biochar, from 78% to 92% for Dry 275 biochar, and from 56% to 83% for Dry 300 biochar. A 25% HTC 260 biochar addition to engineered pellets further improves pellet durability for Dry 275 and Dry 300 combination pellets. Addition of HTC 260 from 25% to 50% increased Dry 250 and Dry 275 biochar pellet durability very little, but did improve pellet durability substantially for Dry 300 and Dry 350. In other words, for a 90% durable engineered pellet 10%, 10%, 25%, and 50% of HTC 260 biochar is required with Dry 250, Dry 275, Dry 300, and Dry 350 biochar, respectively.

To illustrate the effectiveness of HTC 260 biochar addition in engineered pellets, SEM images were taken of Dry 300 biochar pellets with and without HTC 260 additions. SEM images of 100% Dry 300, 90% Dry 300 with 10% HTC 260, 75% Dry 300

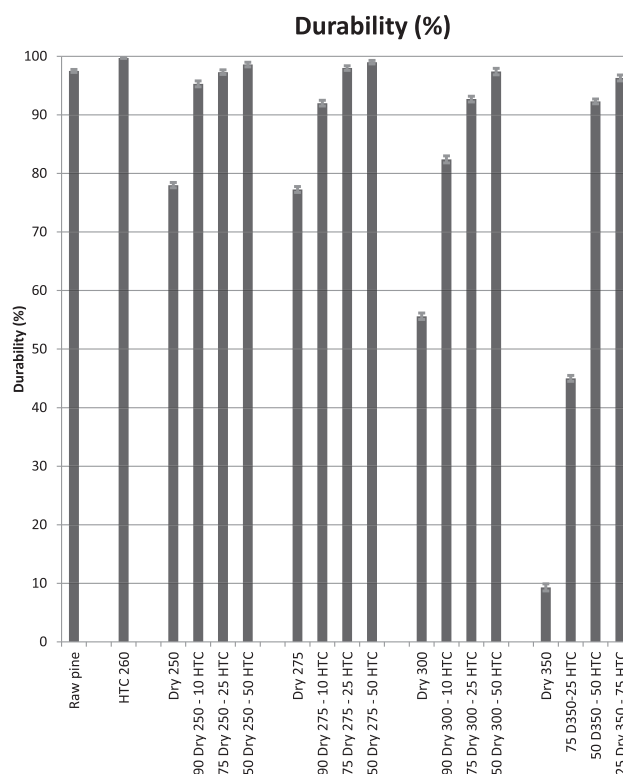


**Fig. 4 – Durability of pellets made from raw pine, from HTC 260, from dry 250, and engineered pellets of various mixtures.**

with 25% HTC 260, and 50% Dry 300 with 50% HTC 260 pellet fractures at two magnifications, 50 and 500 times, are shown in Fig. 5. A 100% Dry 300 pellet (Fig. 5 a, b) shows many cracks and the lack of binder clearly. With addition of 10% (or more) HTC 260 biochar addition (Fig. 5 c,d), the cracks become smaller. Further addition of HTC 260 biochar (25%) makes the particle gap even smaller (Fig. 5 e, f) and this is the stage that the pellet become 93% durable. Increased addition of HTC 260 biochar into Dry 300 pellets appears to cause a void space decrease. Solid bridge type bonding can be observed visibly, particularly in half and half Dry 300 biochar and HTC 260 biochar (Fig. 5 g, h).

Mass density of engineered pellets also increases with increasing HTC 260 biochar proportion. Mass densities of various engineered pellets along with 100% dry biochar are shown in Fig. 6. With a 10% HTC 260 biochar addition, the mass density of Dry 250, Dry 275, and Dry 300 biochar pellets increases by 7%, 1%, and 3%, respectively. But a 50% addition of HTC 260 biochar increases the mass density by 9.7, 6.8, and 11.8%, respectively.

Energy density of engineered pellets depends on several factors, including mass density of the torrefied biochar, HHV of torrefied biochar, and proportion of HTC 260. Fig. 6 shows the energy density of various engineered pellets along with

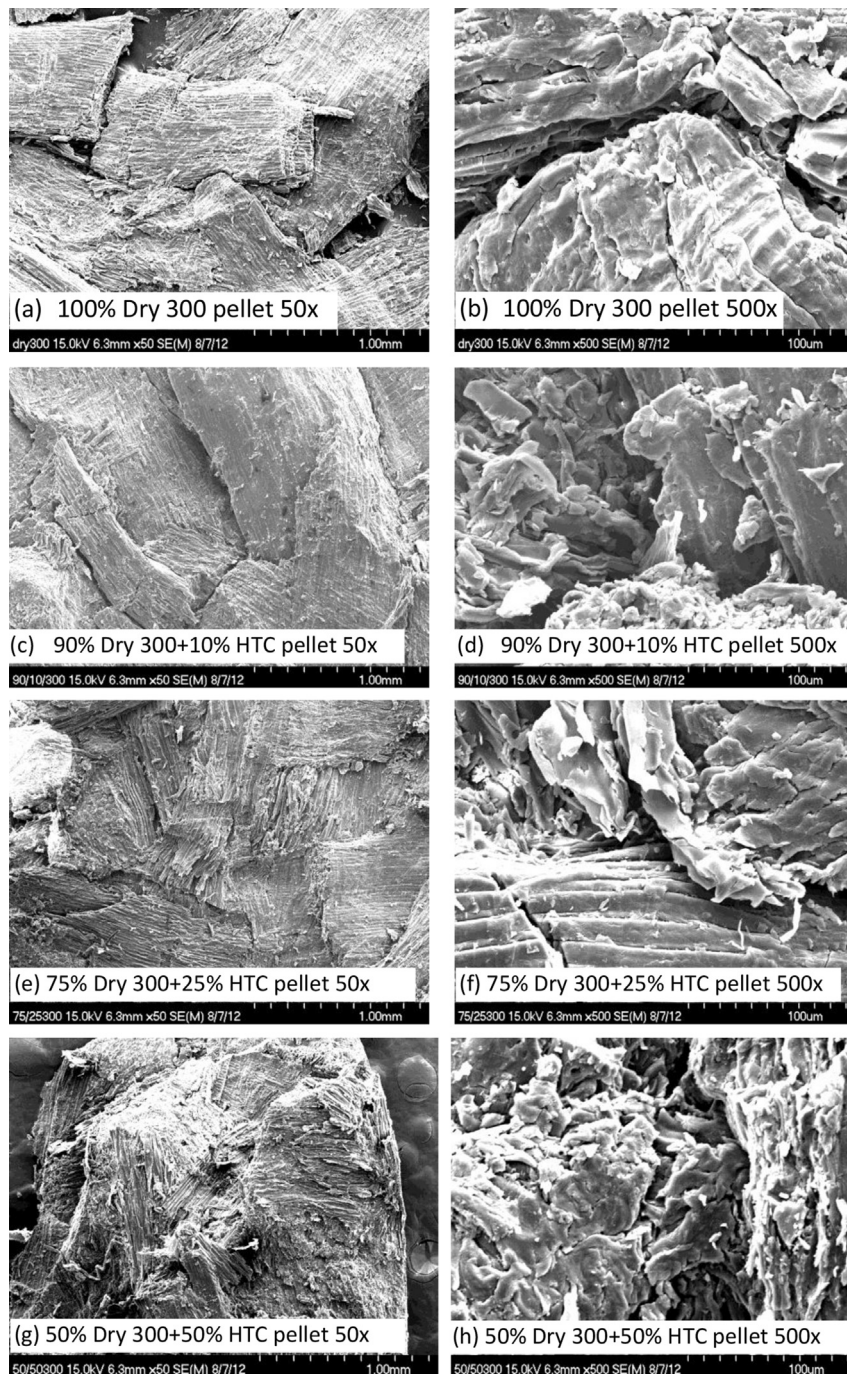


Fig. 5 – SEM images of engineered pellets made from Dry 300 and HTC 260 blends at low and high magnifications.

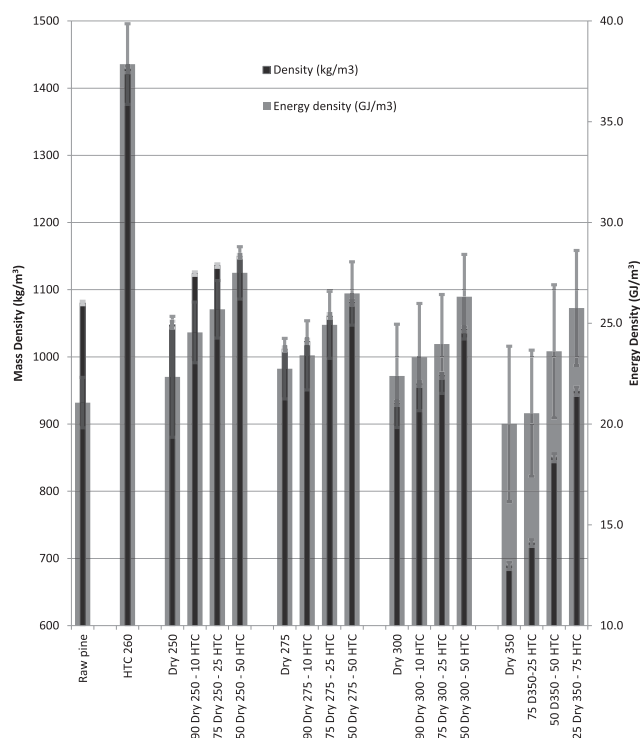


**Fig. 6 – Mass density and energy density of engineered pellets, 100% dry torrefied, 100% HTC 260, and raw pine pellets.**

100% dry torrefied and HTC 260 biochar pellets. As the energy densities of the pure dry torrefied biochars are similar except for Dry 350, it is reasonable that, with the addition of the same amount of HTC 260 biochar, the energy density of corresponding engineered pellets should remain similar. For example, with a 10% addition of HTC 260 biochar, energy densities of Dry 250, Dry 275, and Dry 300 are 24.5, 23.4, and 23.3 GJ m<sup>-3</sup>, respectively. However, for Dry 350 biochar, it takes 50% HTC 260 biochar to yield 23.6 GJ m<sup>-3</sup> of energy density. So, based on energy density considerations, engineered pellets from lower temperature dry torrefaction are preferable, since higher temperature dry torrefaction treatment produces pellets of similar or lower energy density.

#### 4. Conclusions

Dry torrefaction and HTC processes yield a solid biochar product of higher energy value and greater hydrophobicity relative to the originating feedstock. Extractives, hemicellulose, and cellulose content decrease for dry torrefied biochar with increasing dry torrefaction temperature. Dry torrefied biochar is chemically different than raw biomass and HTC biochar, as seen by reduction of aliphatic–OH bonds with increasing temperature. Unlike raw and HTC biochar, no glass transition behavior is apparent in any dry torrefied biochar lignin. Therefore, dry torrefied biochar contains little binder, and pellets show lower durability and lower mass density. Dry 350 biochar pellets are only 9.8% durable and have a mass density of only 689 kg m<sup>-3</sup>. Despite the dry biochar's better

energy value (e.g., 29.0 MJ kg<sup>-1</sup> for Dry 350), the energy density of dry torrefied pellets is lower than even raw pine pellets. HTC biochar is also hydrophobic, of moderate energy value, and has excellent binding capability. An addition of HTC 260 biochar to dry torrefied biochar can produce engineered pellets with better durability, mass density, and energy density than pure dry torrefied pellets. During pelletization, HTC 260 biochar can reduce cracks by making solid bridges among the dry torrefied biochar particles. Engineered pellets are durable and have increased density. Energy density and durability values for engineered pellets imply that dry torrefied biochar treated at torrefaction temperature  $\leq 300$  °C require less HTC 260 binder.

#### Acknowledgments

The authors gratefully acknowledge support by Department of Energy (Contract Numbers: DE-EE 0000272). The authors acknowledge professors Ravi Subramanian from Department of Chemical and Materials Engineering and Steven Spain from Department of Chemistry at University of Nevada for their support on analytical instrumentation. Alexander York and David Graves are greatly acknowledged for the preparation of engineered pellets, and Larry Felix of GTI and Kent Hoekman of DRI are acknowledge for participation in productive conversations.

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